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(54) Tile of the Invention:

MANUFACTURING METHOD FOR DECORATIVE TITANIUM MATERIAL

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Specification

1. Title of the Invention:

MANUFACTURING METHOD FOR DECORATIVE TITANIUM MATERIAL

2. Scope of Claims:

Claim 1.

A manufacturing method for a decorative titanium material, wherein, an optional drawing pattern(s) is drawn on the surface of a clean titanium material using an acid proof resist ink. After it is dried, etching is performed with a mixed acid of nitric acid and hydrofluoric acid. After a sulfuric acid treatment is performed, in addition, coloring is developed by immersing the titanium material into 0.1 – 2.0 % of a hydrofluoric acid solution. After the resist ink layer is removed and the titanium material is dried, it is baked in an oxidized atmosphere.

3. Detailed Explanation of the Invention:

[Industrial Field]

The present invention relates to a manufacturing method for a decorative titanium material, which is used for interior and exterior construction materials, art supplies and household articles and in a wide variety of other fields.

[Prior Art]

Titanium has a small specific gravity and its strength is superior relative to the small specific gravity. Its corrosion resistance is also good. Therefore, it is utilized in various fields as a form of titanium alloy, such as aircraft, ships, various corrosion resistance containers, medical materials, and chemical instruments & equipment.

Conventionally, coloration methods for the purpose of enhancing a decorative effect(s) of pure titanium metal or its alloy have already been disclosed, and it is well known that an anodic oxidization method enables pigmentation of diverse colors among the methods. However, it is also well known that it is impossible to pigmentize a black color even with the anodic oxidization method. Then, for example, as it is mentioned in the publication of Japanese Patent Publication Sho 58 – 23469, a technology, where clean metal titanium is immersed into dilute hydrofluoric acid, which contains 1 % or lower of hydrogen fluoride, and a black coating that is adhered onto the surface of the metal titanium is attempted to be formed, has been developed. Needless to say that the entire surface of the metal titanium becomes black with this method. However, it is extremely difficult to develop an identical black color in each operation, so that the decorative effect(s) cannot be highly evaluated.

[Problems Overcome by the Invention]

As mentioned above, in the prior art, there has been the problem that it is extremely difficult to form a black coating securely adhered onto the surface of pure titanium or titanium alloy without the occurrence of exfoliation and falling away, and, which is a uniform hue, and to enhance a decorative effect(s). The resolution of these problems is the subject of the present invention.

[Problem Resolution Means]

In order to resolve the above-mentioned problems, the present invention has adopted a means for manufacturing a decorative titanium material, where an selective drawing pattern(s) are drawn on a surface of a clean titanium material using a resist ink that is acid proof. After it is dried, etching is performed with a mixed acid of nitric acid and hydrofluoric acid. After a sulfuric acid treatment is additionally performed, coloring is developed by immersing the titanium material into 0.1 – 2.0 % of hydrofluoric acid solution; and, after the resist ink layer is removed and the titanium material is dried, it is baked in an oxidized atmosphere. The details shall be described hereafter.

At first, concerning the titanium material in the present invention, the material is pure metal titanium or alloys where the titanium is a principal component, and these are molded by

processing to be a cold-rolled material, an acid pickling material, a shot material (GBB), an anodic oxidization material, a mirror plane material or a hairline material, or, by other various processing.

Because the surface of the above-mentioned titanium material is considerably polluted by oils and/or dust, it is necessary to be sufficiently cleaned using a normal method, such as alkali cleaning, acid pickling, or rinsing with water, in advance.

Next, an optional drawing pattern(s) (regardless of positive and negative features) is drawn on the surface of the clean and dried titanium material using a resist ink that is acid proof (such as, X – 77 manufactured by Taiyo Ink Mfg. Co., Ltd.), and the drawing pattern(s) are dried, for example, by ventilating air at 70 – 150 °C for 2 – 3 minutes.

The titanium material where the drawing pattern has been drawn as mentioned above is immersed (for example, at 20 – 40 °C, for 3 – 4 minutes) into mixed acid (for example, a water solution that contains 20 % of nitric acid and 7 % of hydrofluoric acid), and etching is performed on portions except for the inked portions that have been drawn using the resist ink. The portions eroded by the etching become lower due to the liquation of the titanium material, and these are colored black to some extent. However, the coloring is insufficient and it is also unstable, so that the following process will be continuously performed, in addition.

More specifically, as a preliminary treatment for a formal coloring processing, the titanium material where the above-mentioned etching has been completed is immersed in sulfuric acid. For the sulfuric acid on this occasion, it is preferable that the concentration be within the range of 15 % through 35 % and the temperature within the range of 60 °C through 80 °C, and the time period for immersion is for approximately 2 – 3 minutes, normally. The preliminary treatment with sulfuric acid is essential for the succeeding coloring process, and when treatment is not performed, coloring becomes unstable and a sufficient effect cannot be demonstrated.

Standard coloring treatment is performed to titanium material where preliminary treatment with sulfuric acid has been completed. This coloring treatment immerses the titanium material into a solution that contains 0.1 – 2.0 % of hydrofluoric acid at 5 – 25 °C of temperature for approximately 3 – 4 minutes. Here, when using a dilute acid where the concentration of the hydrofluoric acid is less than 0.1 %, the coloring becomes unstable, and when the concentration is in excess of 2.0 %, even though the coating is formed and black color is developed once, if the immersion continues, the formed coating is eliminated and the color becomes whitish again, which is not preferable.

The formed black coating is extremely unstable only with this coloring treatment, and it exfoliates and falls away by merely rubbing the surface with a fingertip. Hence, it is important to successively dry the coating. The conditions for this drying are not limited.

However rapid drying should be avoided and it is preferable to gradually dry the coating in the vicinity of, for example, 70 °C.

Then, when the drying is complete, in order to remove a drawing pattern that has been drawn with resist ink, the coating of the resist ink on the surface of the titanium material is wiped off/ removed with an appropriate solvent or with a solution of caustic soda (for example, 15 %).

The titanium material where the above-mentioned treatment has been completed is baked in an oxidization atmosphere in order to further complete the coating drying, the hue stabilization and the coating fixation. Concerning the baking conditions on this occasion, in a normal case, if the temperature is within the range of 300 °C through 350 °C in the air and the baking time is for 2 – 3 minutes, it can be applied even for mass production. Here, it is presumed that the coating is a blackish brown oxidized coating, equivalent to TiO_2, and as long as the conditions are normal for the formation of this type of oxidized coating, the above-mentioned baking conditions will persist.

[Operation]

This method for the present invention is the one where, after the cleaned surface of the titanium material is etched with the mixed acid solution, which contains nitric acid and hydrofluoric acid, a preliminary treatment is performed with warmed dilute sulfuric acid. In

addition, coloring treatment is performed with a well-known hydrofluoric acid solution. Subsequently, the titanium material is baked, resulting in the increase of adhesion and oxidization of the blackish brown coating. Therefore, it is possible to stabilize the hue of the coating and to prevent exfoliation and falling away.

[Embodiment]

A minute indeterminate form spot pattern(s) is printed with a resist ink (X – 77 manufactured by Taiyo Ink Mfg. Co., Ltd.) on a dried surface of a cold-rolled metal titanium material (length: 80 mm, width: 100 mm, thickness: 0.4 mm) where degreasing with a detergent, rinsing with water and cleaning have been performed, and the titanium material is dried by ventilating heated air at approximately 100 °C for approximately 3 minutes. This metal titanium material where printing and drying have been completed is immersed into mixed acid solution (25 °C) that contains 20 % of nitric acid and 7 % of hydrofluoric acid for approximately 4 minutes, and then etching is performed. The metal titanium material where the etching has been completed occurs is colored to blackish brown. However, this it is not sufficient, so that spinning is performed well and the metal titanium material is immersed into heated dilute sulfuric acid (70 °C) with a 25 % of concentration that has been separately prepared for approximately 3 minutes. The metal titanium material where this immersion treatment has been completed is immersed into a solution that contains 1.0 % of hydrofluoric acid for approximately 3 minutes & 30 seconds, and the coloring of blackish brown is confirmed. After the coloring treatment, the metal titanium material is extracted, and after it is dried in a drier at approximately 70 °C for

approximately 5 minutes, the resist ink is wiped off/ removed with a solvent; and then, depressions of 10 – 20 μm are formed by the etching processing on the portions except for the printed pattern area using the resist ink, and the depression portions are colored with blackish brown. However, these colored portions have an insufficient hue and the adhesive property to the metal titanium material is also insufficient, so that it is inserted into an air furnace and baked at approximately 330 ± 5 °C for approximately 3 minutes, thereby promoting the oxidization of the blackish brown coating. The blackish brown pattern with a further stable hue is formed on the resultant metal titanium material, and the blackish brown coating is not one that is easily exfoliated and falls away. Furthermore, after the same operations are newly repeated to nine of the same type of metal titanium materials, decorative metal titanium materials 1 as shown in Fig. 1 and Fig. 2 are obtained. There is no different hue observed on blackish brown color development layers 2, which are formed on the surfaces of a total of ten obtained metal titanium materials, and no exfoliation and falling away easily occurs and these are stable.

Furthermore, for the purpose of confirming that the method in the present invention is superior, a prototype based upon a method, disclosed in the above-mentioned publication of Japanese Patent Application Sho 58 – 23469 is produced. The material used is a cold-rolled metal titanium material, which is the same material and same shape as that of the embodiment, where cleaning has been completed. Ten pieces of the metal titanium material are individually immersed into a solution that contains 1.0 % of hydrofluoric acid for approximately 3 minutes & 30 seconds, and the coloring of blackish brown is confirmed,

so that the operations to extract the metal titanium materials from the solution and to dry them in a dryer at approximately 70 °C are repeated. No printing using a resist ink and no etching treatment are performed of the ten obtained blackish brown coloring layers 2, so that it is natural that no decorative effect(s) due to the pattern and concave & convex contours should emerge. Hence, the hue of the blackish brown color does not easily coincide and unevenness is strikingly remarkable. Hence, the blackish brown color development layers 2 are easily scratched and the surface of the metal skin easily appears.

[Efficacy]

The decorative titanium material that can be obtained with the above-mentioned method in the present invention has a blackish brown color development layer where the hue is uniform, and the color development layer has also stable adhesion properties without easy exfoliation and falling away. Therefore, it can be widely utilized for interior & exterior construction materials, such as ceiling material, wall material or roofing material, frame material for bicycles; body material for vehicles; material for household articles, such as desks or chairs; art supplies and in any other industry fields.

4. Brief Explanation of Drawings:

Fig. 1 is a plane view that shows the decorative titanium material that is produced in the embodiment for the present invention, and Fig. 2 is a cross sectional view of A – A in Fig. 1.

1 ... decorative titanium material

2 ... color development layer

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FIG. 1

FIG. 2

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⑫公開特許公報(A)　平3−153880

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審査請求　未請求　請求項の数 1　(全4頁)

⑤発明の名称　装飾用チタン材の製造方法

⑳特　願　平1−294404
㉒出　願　平1(1989)11月13日

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明　細　書

1．発明の名称

装飾用チタン材の製造方法

2．特許請求の範囲

(1) 清浄なチタン材表面に耐酸性レジストインキによる任意の図柄模様を描き、乾燥後硝酸およびフッ化水素酸の混酸によってエッチングし、さらに硫酸処理を行なった後、フッ化水素酸0.1〜2.0%水溶液に浸漬して発色させ、レジストインキ層を除去し乾燥させた後、酸化雰囲気下で焼成することを特徴とする装飾用チタン材の製造方法。

3．発明の詳細な説明

〔産業上の利用分野〕

この発明は内外装用建築材料、美術材料、什器その他広い分野で利用される装飾用チタン材の製造方法に関するものである。

〔従来の技術〕

チタンは比重が小さく、その割には強度に優れ、かつ耐食性もよいので、チタン合金として航空機、船舶、各種耐食性容器、医科用材料、化学機器具など各方面に利用されている。

従来、純チタン金属またはその合金の装飾効果を高めるための着色法が既に開示されていて、なかでも陽極酸化法によって多種多様の色彩を付けることが可能になったことはよく知られている。しかし、陽極酸化法によっても、黒の着色は不可能であることもよく知られている。そこで、たとえば特公昭58−23469号公報に記載されているように、清浄な金属チタンをフッ化水素1重量パーセント以下の希フッ化水素酸に浸漬し、金属チタン表面に密着した黒色の被膜を形成させようとする技術も開発されたものの、この方法では金属チタンの全面が黒色化することは勿論であるが、操作ごとに同一の黒を発色させることはきわめて困難であって装飾効果を高く評価するわけには行かない。

〔発明が解決しようとする課題〕

以上述べたように、従来の技術においては、純金属チタンまたはその合金の表面に、剥離、脱落等を起こすことなく安定して密着し、しかも一定

した色相の黒色被膜を形成し、装飾効果を高めることはきわめて困難であるという問題点があり、これを解決することが課題であった。

〔課題を解決するための手段〕

上記の課題を解決するために、この発明は、清浄なチタン材表面に耐酸性のあるレジストインキによる任意の図柄模様を描き、乾燥後硝酸およびフッ化水素酸の混酸によってエッチングし、さらに硫酸処理を行なった後、フッ化水素酸0.1～2.0％水溶液に浸漬して発色させ、レジストインキ層を除去し乾燥させた後、酸化雰囲気下で焼成し、装飾用チタン材を製造する手段を採用するものであり、以下その詳細を述べる。

まず、この発明におけるチタン材は材質が純金属チタンおよびチタンを主成分とする合金類であり、これらの冷延材、酸洗材、ショット材(GBB)、陽極酸化材、鏡面材、ヘアーライン材その他各種の加工処理を受けて成形されたものである。

このようなチタン材の表面は油脂類、ごみなどでかなり汚染されているので、アルカリ洗浄、酸洗い、水洗等、通常の方法で充分に清浄化しておく必要がある。

つぎに、清浄化され、乾燥されたチタン材表面に、耐酸性レジストインキ（たとえば太陽インキ製造社製：K-77）を用いて任意の図柄模様（陰陽を問わず）を描き、たとえば70～150℃の風を2～3分間通しながら図柄模様を乾燥する。

このように図柄模様が描かれたチタン材を、混酸（たとえば、硝酸20％、フッ化水素酸7％の水溶液）に浸漬（たとえば20～40℃、3～4分）してレジストインキで描いた画線部以外のエッチングを行なう。このエッチングによって、浸食される部分はチタン材の溶出によって低くなり、微分黒く発色するが、その発色は不充分であり、しかも不安定であるので、さらに、つぎのような処理を継続して行なう。

すなわち、正式な発色処理を行なう前処理として、上記のエッチングを終了したチタン材を硫酸に浸漬するが、この際の硫酸は濃度15～35％、60～80℃のものが好ましく、浸漬時間は通常2～3分程度である。このような硫酸による前処理は後続する発色処理には不可欠のものであり、この処理を行なわないときは、発色が不安定となり充分な効果を出し得なくなる。

硫酸による前処理が終わったチタン材に対して本格的な発色処理を施す。この発色処理はフッ化水素酸0.1～2.0水溶液に温度5～25℃で3～4分程度浸漬すればよい。ここで、フッ化水素酸濃度が0.1％未満の希酸では発色は不安定であり、また2.0％を越える濃度では、一度は、皮膜が形成されて黒色が発色しても、浸漬を続けるとその皮膜がなくなり再び白っぽくなってしまうので好ましくない。

このような発色処理をしたのみでは、生じた黒色皮膜はきわめて不安定で、表面を指先でこすっただけで容易脱落するので、引き続き乾燥することが大切である。この乾燥の条件は特に限定するものではないが、急激な乾燥を避け、たとえば70℃付近で徐々に実施するのが好ましい。

そして、乾燥が終わると、レジストインキで描かれた図柄模様を除去するために、チタン材表面のレジストインキの皮膜を適当な溶剤または苛性ソーダ（たとえば15％）の溶液などで拭き取る。

上記の処理を終わったチタン材は、最後に、皮膜の乾燥、色相の安定化、皮膜の定着化を一層完全なものとするために、酸化雰囲気中で焼成される。この際の焼成条件は、通常の場合、空気中において、300～350℃、2～3分であれば、量産にも充分対応できるものといえる。ここで、皮膜は TiO_2 に相当する黒褐色の酸化物皮膜であると推定されるので、このような酸化物皮膜が生成される条件であれば、上記焼成条件に固執されるものではない。

〔作用〕

この発明の方法は、チタン材の清浄な表面を硝酸およびフッ化水素酸の混酸水溶液でエッチングした後、さらに加温希硫酸で前処理し、公知のフッ化水素酸水溶液による発色処理を行ない、その後に焼成によって黒褐色皮膜の密着力、酸化などを増進させるものであるから、皮膜の色相の安定

化および剥離、脱落等の防止が可能になる。

〔実施例〕

洗剤で脱脂し、水洗して清浄化した金属チタン冷延材（縦80㎜、横 100㎜、厚み 0.4㎜）の乾燥表面に、レジストインキ（太陽インキ製造社製：K-77）で微小な不定形の点模様を印刷し、約100℃の加熱空気を通しながら約3分間乾燥した。この印刷および乾燥を終えた金属チタン材を硝酸20%、フッ化水素酸7%の混酸水溶液（25℃）に約4分間浸漬し、エッチングを行なった。エッチングの終わった金属チタン材は黒褐色に発色はしているものの不充分であるため、よく水切りを行なって、別途準備した濃度25%の熱希硫酸（70℃）に約3分間浸漬した。このような浸漬処理を終えた金属チタン材をフッ化水素酸1.0%水溶液中に約3分30秒間浸漬し、黒褐色の発色を確認した。発色処理後、金属チタン材を取り出し、約70℃の乾燥器中で約5分間乾燥させた後、レジストインキを溶剤で拭き取ったところ、レジストインキの印刷模様以外の部分には、エッチング処理によって10～20㎛程度の窪みが出来、その窪み部分が黒褐色に発色していた。しかし、この発色部分は色相も、また金属チタン材への密着性も不充分であるため、約 330±5℃の空気炉中に約3分間投入して焼成し、黒褐色皮膜の酸化促進を行なった。得られた金属チタン材にはより一層安定した色相の黒褐色の柄が形成され、その黒褐色皮膜は容易には剥離、脱落するものではなかった。なお、これと同じ操作を新たに9枚の同質の金属チタン材に対して繰り返し試みたところ、第1図および第2図に示すような装飾用金属チタン材1が得られた。得られた合計10枚の金属チタン材の表面に形成された黒褐色の発色層2の色相には差異は見られず、また剥離、脱落も容易に起こることなく安定していた。

なお、この発明の方法の優れていることの確認のため、前記の特公昭58－234699号公報に開示された方法に基づく試作品を作製した。使用した素材は実施例と同質、同一形状の清浄化を終えた金属チタン冷延材である。この金属チタン材を10枚個別にフッ化水素酸1.0%水溶液に約3分30秒間浸漬し、黒褐色の発色を確認たので、液から取り出し、約70℃の乾燥器中で乾燥するという操作を繰り返した。得られた10枚の黒褐色の発色層2はレジストインキによる印刷およびエッチング処理を施してないために、模様および凹凸による装飾効果の現れないことは当然であるが、黒褐色の色相が容易に一致せず、著しくむらが目立ち、また黒褐色の発色層2は引掻き傷がつきやすく、容易に地肌を現わした。

〔効果〕

以上述べたこの発明の方法によって得られる装飾用チタン材は色相の一定した黒褐色の発色層を有し、しかもその発色層は容易には剥離、脱落することなく安定した密着力を有していたので、天井材、壁材、屋根材など内外装用建材を始めとし、自転車のフレーム用材、車輌類の車体用材、机、椅子等の什器用材、美術用材その他あらゆる産業分野にわたって広く利用できるものといえる。

4．図面の簡単な説明

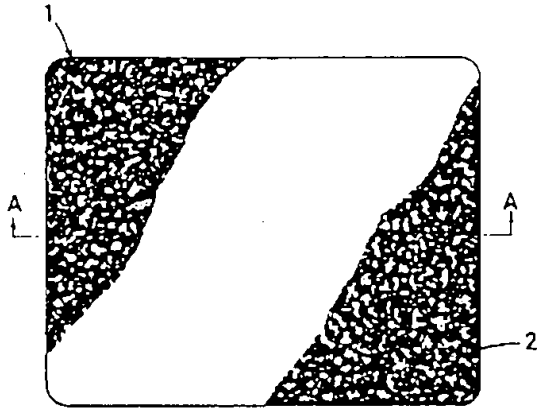
第1図はこの発明の実施例において製作した装飾用チタン材を示す平面図、第2図は第1図のA－A断面図である。

1……装飾用チタン材、　2……発色層。

特許出願人　　株式会社ティグ
同　　山出興産株式会社

同代理人　　雄田文二

第1図



第2図